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Macroscopically interconnected hierarchically porous carbon monolith by metal-phenolic coordination as an sorbent for multi-scale molecules

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ABSTRACT

This study reports on a simple and efficient strategy to prepare macroscopically assembled nanostructured porous carbon (MNPC) based on metal-phenolic interactions. The abundant coordination sites contained in tannic acid enable to form a stable, interconnected hydrogel dough. The porosity evolution mechanism during carbonization process is studied by temperature programmed desorption-mass spectroscopy. Hierarchical pore structure of the MNPC can be developed by modulating the zinc chloride content. The resulting material provides versatile adsorption behaviors for various ranging from small gas molecules to larger molecules such as dye, oil and organic solvents.

1. Introduction

Nanostructured porous carbon materials (NPC) have attracted considerable attention in various research fields [1,2]. Due to high specific surface area (SSA), tunable pore structure, extraordinary chemical/thermal stability, and electrical properties, NPC have been employed in particular to address emerging energy and environmental problems [3–7]. To extend their practical values, numerous studies have been exploited to manufacture macroscopically assembled NPC (MNPC) without losing their original properties [8–10]. One of the common strategies in synthesizing the MNPC is the carbonization of organic precursor aerogel based on sol-gel chemistry [11–14]. In addition, carbon nanomaterials, such as carbon nanotube and graphene (1D and 2D building units, respectively), can function as building blocks to form the MNPC [15–19]. These strategies allowed for the preparation of various MNPC with high SSA and mechanically stable 3D structures. However, these approaches required time-consuming, complicated, and environmentally tough steps like the freeze-drying process, physicochemical activation, template removal, and several washing steps.

Tannic acid (TA) is a polyphenolic biomolecule, which can be extracted easily in plants, tea, and berries. The abundant phenolic groups on TA show chelating behaviors with diverse metal ions and form a stable compound on the nano- and microparticle surface [20–22]. Inspired by this coordination chemistry, we report on a simple and facile method to prepare the MNPC analogous with bread. Due to numerous coordination possibilities in a widely populated large area of TA, the hydrogel can build a stable, interconnected network during hydrothermal reaction. Therefore, hydrogel dough can be simply dried on the hot plate without time- and cost-consuming drying step. In addition, Zn ion was utilized as metal ion to obtain MNPC with hierarchical pore structure. The stable TA-Zn hydrogel developed pore structure through similar mechanism with the case of MOF-derived porous carbon (MDC) during carbonization [23]. Furthermore, Zn species can develop micropore by carbothermal reduction during carbonization [24]. The resulting MNPC monolith resembling bread with a unique pore structure exhibits versatile adsorption capabilities when evaluated as sorbents for molecules at various scales from small gas

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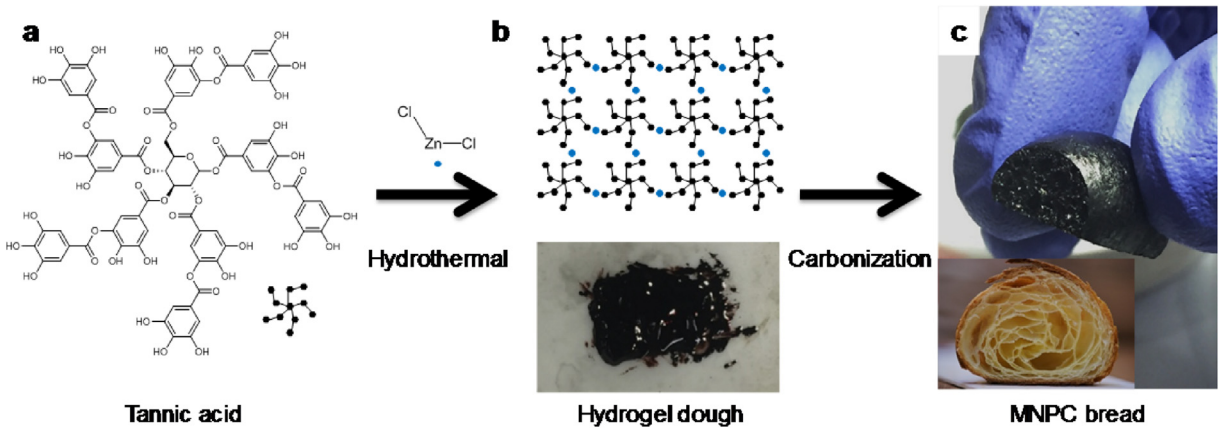

Fig. 1. Schematic illustration displaying the MNPC preparation process. (a) Chemical structures of TA with abundant phenolic groups. (b) Hydrogel dough resulted from metal-phenolic interactions after hydrothermal reaction. (c) Cross-sectional surface image of the MNPC resembling croissant (inset) after carbonization. (A colour version of this figure can be viewed online.)

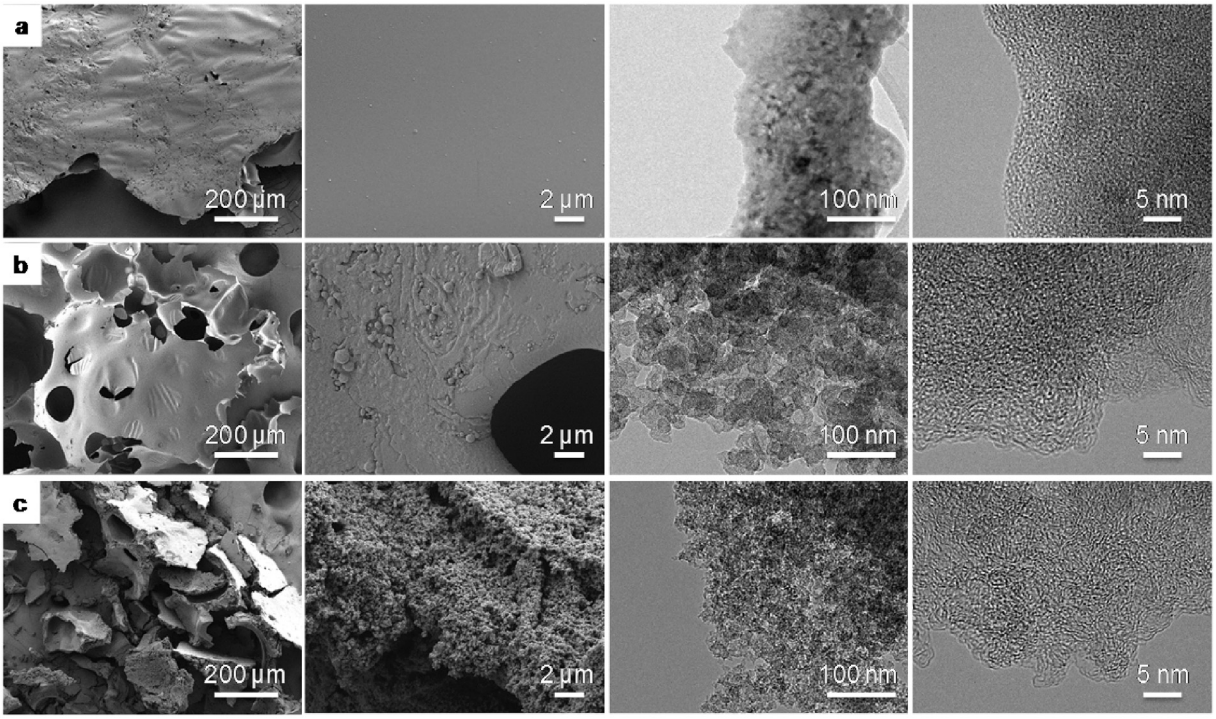

Fig. 2. SEM and HRTEM micrographs of the (a) TA, (b) TZC1, and (c) TZC5.

molecules to larger molecules, such as oils and toxic chemicals.

2. Experimental

2.1. Preparation of the MNPC

200 mg of TA (Sigma-Aldrich) were dissolved in distilled water (20 ml) in a vial, which was then mixed with zinc chloride (Sigma-Aldrich). The final ratio of TA and zinc chloride was 1:0, 1:0.5, 1:1, 1:5, and 1:10 by weight and denoted by TA, TZC05, TZC1, TZC5, and TZC10, respectively. The reaction mixture was transferred to a Teflon-lined autoclave (50 ml) and heated at 160 °C for 8 h. After cooling to room temperature, the resulting black suspension was dried on the heating plate at 100 °C for 12 h to vaporize the water. The materials were transferred to a box furnace and were heat-treated at 900 °C under nitrogen with a heating rate of 10 °C/min to pyrolyze the organic species. After reaching the target temperature, the materials held for 1 h and then cooled to room temperature. The resulting materials were washed with 0.1 M HCl solution (200 ml) to remove the remaining metal ions. This was followed by repeatedly washing with ethanol and drying to obtain the final products.

2.2. Characterization

Scanning electron microscopy (SEM) (MERLIN Compact) and high-resolution transmission electron microscopy (HRTEM) images were used to analyze the surface morphology of the products. The powder X-ray diffraction (XRD) profile was recorded by using a Bruker D8 Advance diffractometer equipped with nickel filtered Cu